

Colouring of ceramics by means of ionic or complex-
containing solutions

125 A
JPB 1
7 B'
5 The invention relates to the colouring of ceramics by means of ionic or complex-containing solutions. The invention relates in particular to the colouring of dental ceramics based on zirconium oxide by means of solutions of rare earth metals and subgroup elements.

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15 Ceramics are much valued, because of their physical properties, in the construction of high-quality dentures. Aluminium and zirconium oxide ceramics have long been the materials of choice in the medical field (Reprint from Industrie Diamanten Rundschau, IDR 2/1993, "Aluminium- und Zirkonoxidkeramik in der Medizin"). There are a number of publications in the dental field which deal with the use of ceramics for the preparation of prostheses. Various ceramic systems are also already available on the dental market
20 (CEREC, Fa. Siemens; Procera, Fa. Nobel-Biocare).

In the dental field in particular, however, it is not only the mechanical parameters that play a major role, but also specially the aesthetics. Translucence and coloration of
25 the framework or facing ceramics are important, in order to allow the patient to achieve a natural appearance for his dentures.

Dentures are normally prepared from a framework and a
30 facing.

In the case of the systems known up until now, only a superficial individual colouring of the basic framework can be carried out by the dental technician, the aesthetic design possibilities being limited.

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In order to achieve a natural appearance of the prosthesis, the tooth colour and the translucence must be simulated over several layers, beginning with the framework.

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The natural appearance of a prosthesis is guaranteed by as high as possible a free path length $z = x + y + m$ of the incident light through the layer (x) of the facing ceramic and the layer (m) of the framework ceramic and optionally an intermediate layer (y).

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In order to change the basic shade of the framework ceramic, conventional systems must work with colouring intermediate layers, for example opaquer liners, which display no, or greatly reduced, translucence; the free path length of the light decreases by the thickness of the framework ceramic (m) and of the intermediate layer (y) to $z = x$. A description of this procedure can be found in e.g. the instructions issued by Vita for the use of the Vita-Dur system □ or by DUCERA for the ALL Ceram system.

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Such systems use, as intermediate layer, dye pastes or dye suspensions, which are applied to the framework by the dental technician in several procedures and are finally fired in the oven.

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This process is not only time-consuming, but also cost-intensive.

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The object of the invention is thus to provide a system for the colouring of ceramics, in particular ceramic dentures, which guarantees an optimum aesthetic appeal with minimal
5 outlay on labour and with costs reduced to the minimum.

Surprisingly, this object is achieved by a process for the colouring of ceramics in the porous or absorbent state, which is characterized in that the ceramics are translucent
10 and metal ion solutions or metal complex solutions are used for the colouring. Solutions preferred for this contain defined concentrations of at least one of the salts or complexes of the rare earth elements or the elements of the subgroups.

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15 The solutions are preferably water- or alcohol-based. Suitable salts or complexes are preferably those from the group of the rare earths or the 2nd or 8th subgroups, in particular Pr, Er, Fe, Co, Ni, Cu.

20 Salts or complexes with inorganic opposed ions such as e.g. Cl^- , Br^- , J^- , SO_4^{2-} , SO_3^{2-} , NO_2^- , NO_3^- , ClO_4^- , ONC^- , SCN^- , are preferred, which can also mean oxo complexes of acid or basic salts, but not double salts with an element of the
25 1st or 2nd main groups. Furthermore, salts or complexes with organic ions or ligands are preferred which contain 1 to 30 C atoms and from 1 to 10 heteroatoms, such as O, N, S. In detail, these are alkoxides or salts of organic acids. Preferred here among the alkoxides are the salts of
30 the C_1 - C_{10} -alkanols, in particular the methoxides, ethoxides, n- and i-propoxides and n-, i-, sec. or tert.-butoxides. Among the salts of organic acids, those of

mono-, di- and tri-C₁-C₂₀-carboxylic acids are preferred, in particular formate, acetate, malate, maleate, maleinate, tartate, oxalate. Finally, the ligands are also taken to include complexing agents serving to stabilise the metal salts in their oxidation stage and in solution. These can be organic C₂-C₂₀ molecules with up to 10 hetero atoms, O, N or S, including in particular EDTA and its salts, NTA, salicylic acid, phenols, 5-sulphosalicylic acid etc.

10 Aqueous or alcoholic solutions of Pr, Er, Fe, are preferred, for example as chlorides, acetates or alcoholates.

The ions or complexes are preferably used in concentrations of 0.0001 to 15 wt.-%, particularly preferably from 0.001 to 10 wt.-% and quite particularly preferably from 0.01 to 7 wt.-%.

By ceramics and dental ceramics are meant here all high-strength oxides of the elements of the main groups II, III and IV and the subgroups III and IV as well as their mixtures, in particular Al₂O₃, ZrO₂, both partly and also fully stabilised, MgO, TiO₂ and their mixtures. In particular, translucent ceramics are taken to be covered by the term ceramics and dental ceramics.

Furthermore it is surprising that the depth of colour of the colouring is not dependent on the action time of the solution but only on its concentration. This is particularly advantageous, as the dental technician is not tied to action times accurate to within a few seconds, but can perform his work within certain tolerances for as long

as is desired with the solutions according to the invention. The action time of the solution can in theory be as long as desired. It depends only on other effects in the solution, for example pH-value changes or the release of
5 ions, which can hinder the colouring process. The result is generally an action time, until the depth of colour of the colouring does not change, of a few hours. The action time is preferably under 2 hours, in particular under 1 hour and particularly preferably under 20 minutes.

10 Advantageously, the above mentioned intermediate layer (y) can be completely dispensed with thanks to the present invention, as the framework ceramic can already be individually coloured by the solutions according to the
15 invention. An additional cost- and time-intensive step of the firing of the intermediate layer is therefore dispensed with. Only the free path length $z = x+y+m$ is available to the incident light, as the path is no longer interrupted by the intermediate light.

20 The solutions according to the invention can also contain, alongside the salts or complexes of the rare earth elements or the subgroup elements, stabilising agents, such as complexing agents, grinding auxiliaries as well as organic
25 dye stuff pigments to facilitate the matching of the colour by the dental technician.

Complexing agents, such as ethylenediaminetetra acetic acid, are suitable as stabilising agents. Grinding
30 auxiliaries are taken to include for example temporary binders and thixotropy agents, such as polyglycols,

polysaccharides, polyethylene glycols, polyvinyl alcohols, hydrogenated castor oils.

Due to the low concentrations of colouring ions or
5 complexes within the solutions according to the invention
and the associated poor optical recognizability of the
applied shade, organic pigments can also be added to
facilitate the matching of colour by the dental technician.
These additives are particularly helpful during the
10 application of the solutions to specific areas by means of
application instruments. The additives are to be chosen so
that they are destroyed without leaving any residue upon
the firing of the prosthetic work.

15 The solutions according to the invention can be applied in
the following ways to the pre-sintered or absorbent
ceramics:

1. Immersion of the ceramic in solutions of defined
20 concentrations;
2. Deposition of the solutions to the ceramic by means of
suitable application instruments, for example, brush,
swab;
3. Deposition of the solutions to the ceramic by means of
25 spraying processes.

Wall thicknesses of up to 10 mm, preferably 7 mm, are
thoroughly coloured by means of the process according to
the invention. In particular in the dental field,
30 dimensions of 10 mm, preferably 7 mm, for the diameter of a
workpiece and 7 mm, preferably 5 mm, for the height of a
workpiece are possible in the preparation of crowns and

bridges. These mm values relate to the thicknesses of the colourable wall thickness of the dental workpieces.

Naturally, workpieces outside the limits given here are also contained in the scope of the invention.

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The ceramics are preferably completely through-coloured.

The invention also relates to a kit, comprising

- (i) at least one stock bottle with a metal ion or metal complex solution for the colouring of the ceramics,
- (ii) a receptacle for the colouring, and
- (iii) optionally a screen.

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The invention is explained in detail in the following by means of examples, without thereby limiting it.

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**Concentration-dependent colouring of zirconium oxide
stabilised by 3 mol yttrium oxide**

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For the preparation of the solutions, the corresponding amounts of colour reagent are dissolved in water. Ceramic bodies are steeped in this for 5 minutes and then dried and sintered. The specimens are then ground and polished for the colorimetry. The following parameters form the basis of the colour determination:

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Opacity value O:	Measure of the transparency (0% is completely transparent, 100% is opaque),
L*-value:	Brightness (100: complete reflection; 0; no reflection);

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a*-value: Red-green shift (+a: red; -a: green);
b*-value: yellow-blue shift (+b: yellow; -b:
blue);

- 5 Measuring apparatus: Hunterlab LabScan Spectrocolorimeter;
Measurement method: Cielab (colour), opacity according to
ASTM D2805/TAPPI T425/TAPPI T519.

- 10 To demonstrate the independence of the colour intensity
from the action time of the solution, various action times
are used with a fixed solvent concentration and the colour
determination carried out analogously.

- 15 Commercial zirconium dioxide from Tosoh, Japan of the type
TZ3YE was used as material.

Colouring with Fe(III)Cl₃ solutions

Concentration solution [wt.-%]	L*	a*	b*	0
0	85.67	-0.97	1.51	91.4
0.1	83.93	-1.67	5.15	92.36
0.3	79.04	-1.52	22.35	95.1
0.5	75.37	1.16	25	95.32
0.75	74.01	1.72	25.91	96.51
1	72.25	2.83	24.67	97.79

Colouring with Pr(III) acetate solutions

Concentration solution [wt.-%]	L*	A*	b*	O
0.1	81.02	-3.60	24.98	89.98
0.25	80.80	-3.02	34.17	91.40
0.75	74.85	4.77	47.31	92.11

Result: The intensity of the colour can be controlled via the concentration of the solution.

Dependency of colour intensity on action time

Solution concentration: 0.75 wt.-% Fe (III) Cl solution

Action time	L*	a*	b*	O
2 minutes	75.18	0.32	20.15	96.05
5 minutes	76.06	-0.42	21.4	95.86
10 minutes	75.18	-0.09	22.4	96.08
20 minutes	75.80	-0.21	23.11	96.37

Result: The action time has no effect on the colour intensity.